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Non-linear and non-local behaviour in spontaneously electrical solids

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Abstract

We show that solids displaying spontaneous dipole orientation possess quite general non-local and non-linear characteristics, exemplified through their internal electric fields. The most graphic illustration of this, uncovered originally through electron beam studies, may be found in films of *cis*-methyl formate (*cis*-MF), for which data demonstrated the counter-intuitive property that the degree of dipole order in the film does not monotonically decrease as the temperature of deposition rises, but rather *increases* sharply above ~ 77 K. Here we show how the independent method of reflection-absorption infrared spectroscopy (RAIRS) yields results which bear out this conclusion. These new data confirm (i) that the behaviour of spontelectrics is governed by an expression for the degree of dipole orientation, which is continuous in temperature, but with a discontinuity in the derivative, and (ii) that the temperature of deposition associated with this discontinuity matches the temperature above which dipole order switches from the expected reduction with temperature to an increase with temperature.

1. Introduction

When dipolar molecules are laid down from the gas phase, the resulting films can spontaneously possess strong electric fields normal to the plane of the film, whose magnitude can be $>10^8$ Vm⁻¹.^{1,2,3,4,5} Such films are termed ‘spontelectric’ and are the subject of the present work. The electric field arises through orientation of dipoles within the film, giving rise to a polarization charge on the surface. The phase space in which dipole orientation is observed to occur has the general characteristic of displaying a Curie-like point on warming to some distinctive temperature.³ It is therefore natural to assume that films laid down at increasingly higher temperature, and thus greater thermal agitation, should show less orientation and therefore a lower electric field. This is indeed observed for numerous species, for example N₂O, toluene, propane, *iso*-pentane *etc.*³ Using RAIR spectroscopic data for *cis*-methyl formate (*cis*-MF), we show here that the non-linear and non-local characteristics of the spontelectric state can cause the degree of dipole orientation and electric field to *increase* with increasing temperature of deposition. This strongly reinforces the conclusion based on earlier work,^{2,3} using data from direct measurement of surface polarization potentials, obtained with an electron-beam technique. For ease of reference, data using this technique for the electric field in *cis*-MF are displayed in Fig. 1.² Our present RAIRS results are demonstrated here to match these data and underline very clearly the distinctive non-linear and non-local properties of the spontelectric state of matter.

2. The model for the spontelectric state

A mean field model of the spontelectric state has been described in detail elsewhere³ and is briefly reviewed here, specifically to show the discontinuous nature of the variation of the electric field within spontelectric films with temperature of deposition. The model involves a parametrized electric field in the film of material, in which the net component of the field at any moiety, normal to the

plane of the film, E_z , is written as the sum of a symmetric and an asymmetric part. The symmetric part, related to the ‘local field’ at any molecular site,⁶ very largely dictates the molecular force field and thus molecular vibrational frequencies in the solid, significant for the present RAIRS data. This part of the field is expressed as a constant term plus a dipole-dipole term, proportional to $(\langle\mu_z\rangle/\mu)^2$, representing the average intermolecular dipole-dipole interactions.^{7,8,9} Here, $\langle\mu_z\rangle/\mu$, the degree of dipole orientation, is the ratio of the average z-component of the dipole moment and the total dipole moment of the molecular species in the solid state, where the z-axis is normal to the plane of the film. The asymmetric term, arising from the long-range polarization, or spontelectric, field which permeates the film, is given by $\langle E_{\text{asym}} \rangle \langle\mu_z\rangle/\mu$. The characteristic of the spontelectric state is that $\langle\mu_z\rangle/\mu$ is non-zero. The spontelectric field, $\langle E_{\text{asym}} \rangle \langle\mu_z\rangle/\mu$, acts in opposition to the symmetrical part of the field and represents the field permeating the medium, created by the average dipoles and experienced by an average dipole.

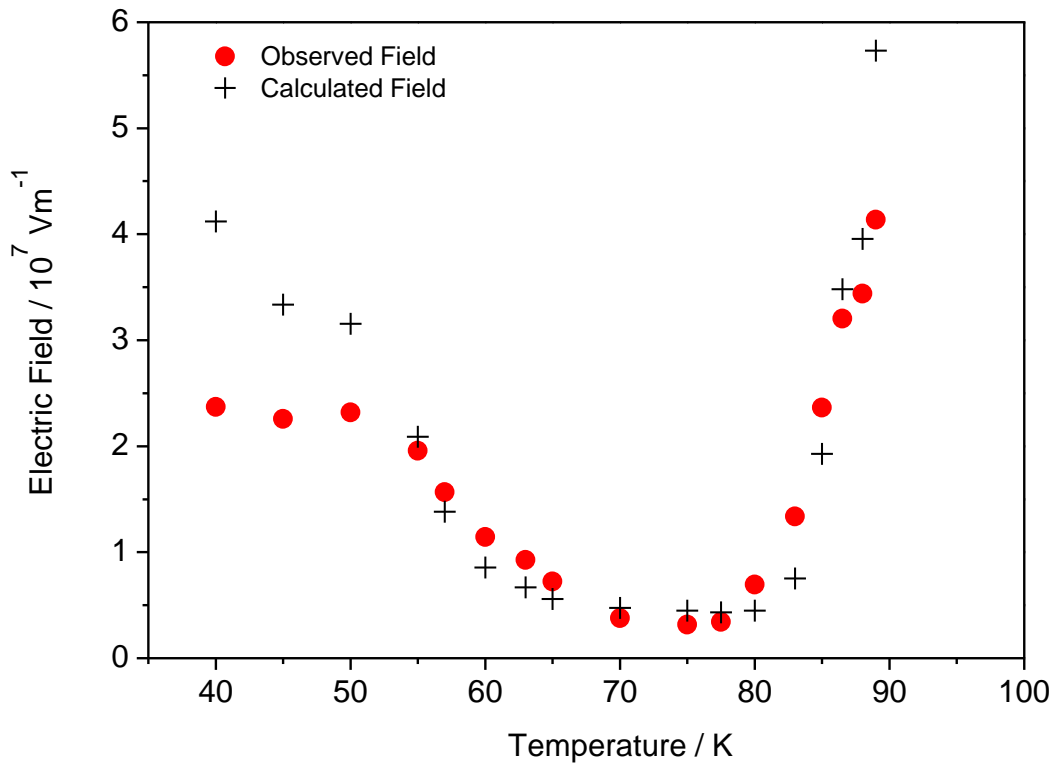


Figure 1: The spontelectric field vs deposition temperature for *cis*-MF.^{2,3} Calculated values are also shown (see text). Systematic errors due to uncertainties in film thickness may yield errors of up to 30% in absolute values of electric fields. Random errors in electric fields vary from 1% at low temperature to 5% at the highest temperatures. Results are taken from ref. 2.

Hence we may write

$$E_z = \langle E_{\text{sym}} \rangle \left[1 + \zeta \left(\frac{\langle\mu_z\rangle}{\mu} \right)^2 \right] - \langle E_{\text{asym}} \rangle \frac{\langle\mu_z\rangle}{\mu} \quad (1)$$

where $\langle E_{\text{sym}} \rangle$, $\langle E_{\text{asym}} \rangle$ and ζ are parameters taken to be independent of deposition temperature, over any temperature range for which there is no abrupt structural change.¹⁰ The $\zeta(\langle\mu_z\rangle/\mu)^2$ term in equation (1) may be interpreted as a measure of the tendency of one dipolar species to restrict the

angular motion of another, a so-called ‘frustration’ term.

Mean field theory gives an implicit expression for $\langle \mu_z \rangle / \mu$, yielding the familiar Langevin function for orientational interactions⁶

$$\frac{\langle \mu_z \rangle}{\mu} = \coth\left(\frac{E_z \mu}{T}\right) - \left(\frac{E_z \mu}{T}\right)^{-1} \quad (2)$$

in atomic units, where T is the deposition temperature of the material. A detailed analysis is given in [3] but suffice it to say here that Eq. 1 and 2 may be combined to yield an explicit expression for $\langle \mu_z \rangle / \mu$, which leads to a total derivative of $\langle \mu_z \rangle / \mu$ vs T as follows:

$$\frac{d \langle \mu_z / \mu \rangle}{dT} = \frac{1/\mu E_z - (\mu E_z / T^2) \operatorname{cosech}^2(\mu E_z / T)}{(\mu E' / T) \operatorname{cosech}^2(\mu E_z / T) - E' / T / \mu E_z^2 - 1} \quad (3)$$

where $E' = \langle E_{\text{asym}} \rangle - 2\zeta \langle E_{\text{sym}} \rangle \langle \mu_z \rangle / \mu$. This total derivative has the property that in the continuous variable T , it possesses a set of discontinuities for a certain critical range of parameters, $\langle E_{\text{sym}} \rangle$, $\langle E_{\text{asym}} \rangle$ and ζ , exemplified by a singular cut in $(T, \langle \mu_z \rangle / \mu)$ space (figure 27 of [3] for *cis*-MF). In this connection, *cis*-MF is presently the only material which we have unequivocally shown to display this singular cut: other materials may of course exist but remain to be found. A general characteristic of equation (3) is a reversal of sign of $d(\langle \mu_z \rangle / \mu) / dT$ on each side of the cut, being negative on the low temperature and positive on the high temperature side. The positive sign causes the increasing degree of orientation with increasing temperature of deposition, implied by the increasing field at $T \geq 77\text{K}$ in Figure 1. Note that the form of equation 3 arises through the inherent non-locality of the model, in the sense that equations 1 and 2 imply that every part of the film communicates with every other part via the electric field, and through the non-linearity of the model, in the sense that the extent to which the dipoles are oriented, $\langle \mu_z \rangle / \mu$, depends on the electric field, which itself depends on the degree of orientation.

3. The case of *cis*-Methyl Formate: RAIRS experiments

Turning specifically to methyl formate, electronic structure calculations show that gas phase *cis*-MF is 19.7 kJ mol⁻¹ more stable than *trans*-MF, at the coupled cluster level of theory¹¹ with single and double excitations (CCSD/aug-cc-pVTZ^{12,13}) in geometry optimizations and frequency calculations, and additional non-iterative triple excitations (CCSD(T)) in single-point energy calculations. Here the CCSD(T) energies were extrapolated to the basis set limit.¹⁴ The value of 19.7 kJ mol⁻¹ may be significantly modified through mutual polarization in the solid, but nevertheless indicates a strong preference for *cis*-MF between 55 K and 90 K, the temperature range which we consider here (see below). No crystallographic data exist in the literature but IR spectroscopy suggests that solid MF exists in two phases: amorphous and crystalline. The onset of crystallization of MF has been reported for temperatures between 90 K and 100 K in transmission¹⁵ and in RAIR spectra¹⁶, signalled by sharpening of the absorption lines above 90 to 100 K. Mutual polarization in the solid also leads to a strong decrease in the effective dipole moment compared with the gas phase, via $\mu = \mu_0 / (1 + \alpha k / s^3)$, where s is the average spacing between successive layers, α is the molecular polarizability, $k = 11.034$ and μ_0 is the gas phase dipole moment of the molecules involved. For *cis*-MF, $s = 0.244$ nm, $\alpha = 5.25 \times 10^{-30}$ m³, $\mu_0 = 0.6949$ au (or 1.766 D), giving $\mu = 0.354$ D.^{2,3}

Fitting data for deposition temperatures between 55 and 75K to equations (1) and (2), yields $\langle E_{sym} \rangle = 1.206 \times 10^7 \text{ V m}^{-1}$, $\langle E_{asym} \rangle = 1.148 \times 10^9 \text{ V m}^{-1}$, $\zeta = 1.45 \times 10^4$. These values then go on to predict the observed qualitatively distinctive rise in the spontelectric field for deposition temperatures $\geq 77\text{K}$, as seen in Figure 1 and in Table 1 for $\langle \mu_z \rangle / \mu$. Below 55K the model fails, most likely due to involvement of a different phase of *cis*-MF at lower temperatures. We therefore limit discussion to temperatures of deposition $\geq 55\text{K}$ and focus upon the anomalous behaviour of *cis*-MF above 75 to 77K. We now present RAIRS data for *cis*-MF for $55 < T < 90\text{K}$ and show that these new data corroborate the counter-intuitive behaviour of the spontelectric field (Figure 1) and the degree of dipole orientation (Table 1).

The use of RAIRS to measure the properties of spontelectric solids is based on the vibrational Stark effect, via the response of molecular vibrations to an electric field in the film. The technique has been validated¹⁷ for N_2O films, through comparison with values of surface potentials and corresponding spontelectric fields obtained using the electron beam technique. In addition, RAIRS studies of the spontelectric effect in solid CO yield spontelectric fields¹⁸ which match those which reproduce spectral shifts in VUV spectra of solid CO.⁵ RAIRS spectra of *cis*-MF films, grown by vapour deposition at various temperatures, were obtained at Heriot-Watt University, using a Fourier-transform infrared spectrometer (Varian 670-IR) in reflection-absorption mode, at a grazing incidence of 75° with respect to the normal to the substrate. The substrate was oxygen-free, high conductivity copper, coated with a 300 nm layer of amorphous silica, whose presence allows the detection of TO modes.¹⁷ Spectra, taken at a resolution of 0.1 cm^{-1} , thus show LO-TO splitting, key for the analysis involving the spontelectric effect. Samples were deposited at a range of temperatures but were cooled to 18K before spectra were recorded, noting that this introduced no distortion into our data, since changes in dipole orientation are not temperature reversible.³ Errors in temperature measurement, performed using a KP-type thermocouple, were $\pm 0.5 \text{ K}$.

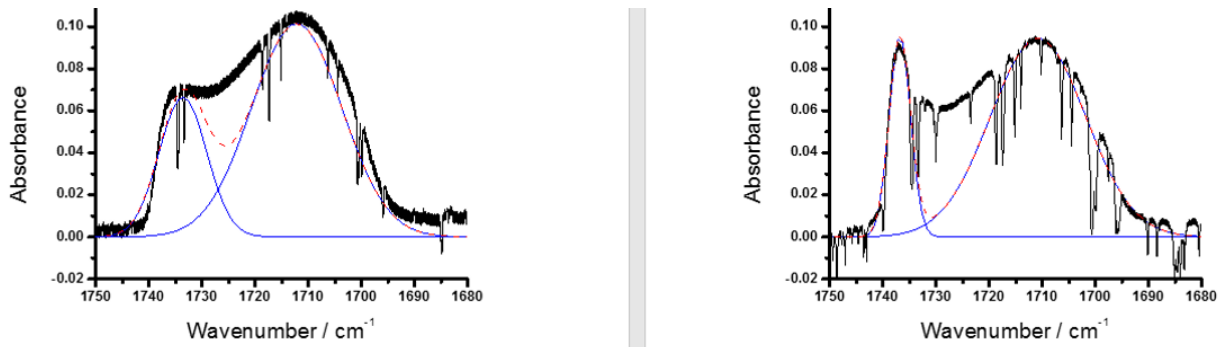


Figure 2: RAIR spectra of solid *cis*-methyl formate deposited on amorphous silica film on a copper surface (black lines). Estimates based on coverage dependence of TPD places the film thickness at a few 10's of ML. The sharp spectral features are due to residual water vapour in the purge gas of our external optics, where features are useful as wavelength markers. Spectra on the lhs were recorded at 70K and on the rhs at 90K deposition temperatures and were obtained by co-adding 512 scans at a resolution of 0.1 cm^{-1} in typically 60 minutes. The blue lines are Gaussian components representing the LO and TO modes in the solid obtained by non-linear fitting using Origin. LO-TO splittings are given in Table 1. The red dashed line shows the sum of the fits, the greater discrepancy at 90K compared with 70K indicating increased disordered molecular structure at higher deposition temperature.

From hereon we consider only the readily identifiable C=O stretching mode and associated LO-TO splitting, which lies between 1733.8 and 1736.8 cm^{-1} for LO and between 1710.8 and 1713.2 cm^{-1} for TO modes. Two typical spectra, at 70K and 90K, focussing on this C=O region in *cis*-MF, are shown in Figure 2. Table 1 demonstrates that the LO-TO splitting rises markedly between 55 and 90 K. The increase in splitting at higher deposition temperatures in Table 1 is sufficient to illustrate a clear general trend of an increasing vibrational Stark effect. Thus RAIRS data immediately provide a

qualitative corroboration of the anomalous deposition temperature dependence of both the spontelectric field and the degree of dipole orientation in *cis*-MF. We now seek to put this on a quantitative footing.

Deposition Temperature / K	LO / cm ⁻¹ (ν_L)	TO / cm ⁻¹ (ν_T)	Splitting $\Delta\nu$ / cm ⁻¹	Degree of dipole orientation
55	1733.8±0.4	1713.2±1.6	20.6±1.6	0.0152
60	1733.6±0.4	1712.8±1.0	20.8±1.1	0.0089
65	1733.2±0.8	1712.0±0.8	21.2±1.1	0.0056
70	1722.7±0.6	1712.0±0.2	21.7±0.6	0.0029
75	1734.8±0.4	1711.6±0.2	23.2±0.4	0.0025
80	1735.6±0.6	1711.6±0.6	24.0±0.8	0.0054
85	1736.4±0.2	1711.4±0.2	25.0±0.3	0.0184
90	1736.8±0.2	1710.8±0.4	26.0±0.4	0.0322

Table 1. Column 1: deposition temperature of *cis*-MF film. Column 2: Longitudinal oscillation (LO) frequency of the CO stretch. Column 3: Transverse oscillation (TO) frequency of the CO stretch. Column 4: measured LO-TO splitting. Column 5: degree of dipole orientation, $\langle\mu_z\rangle/\mu$, from earlier work.^{2,3}

The LO-TO splittings, $\nu_L - \nu_T = \Delta\nu$, in Table 1 arise through a combination of the intrinsically different vibrational frequencies associated with LO and TO modes and, at the level of approximation adopted here, an independent contribution due to the vibrational Stark effect. Thus the observed values of $\Delta\nu$ are the sum of $\Delta\nu_B$, the intrinsic splitting, essentially independent of temperature of deposition, and $\Delta\nu_S$, the spontelectric Stark term, which is a function of temperature through the temperature dependence of the spontelectric field. The intrinsic splitting is determined largely by the size of the unit cell.¹⁹ Initially we assume that this size remains approximately constant with temperature, irrespective of phase change. $\Delta\nu_B$ can then be estimated from spectra of the crystalline phase formed by deposition above 90 K, at which temperatures the solid is no longer spontelectric and there are therefore no spontelectric contributions to the LO-TO splitting. This yields $\Delta\nu_B = 13.5 \text{ cm}^{-1}$.

It has been shown¹⁷ that the difference in energy between TO and LO vibrations divided by the TO vibrational energy, that is, $(U_T - U_L)/U_T$, $\sim \Delta\nu/\nu_T$, where the subscript ‘T’ refers throughout to transverse oscillations and ‘L’ to longitudinal. U_T and U_L are related to quantities governing the spontelectric effect, $\langle E_{\text{sym}} \rangle$, $\langle E_{\text{asym}} \rangle$, ζ and $\langle\mu_z\rangle/\mu$, since these define the environment of the constituent molecules. First, the total field governing ν_T (say) must be proportional to $(\Delta\nu/\Delta\nu_S)\langle E_{\text{sym}} \rangle(1 + \zeta(\langle\mu_z\rangle/\mu)^2)$, where $\Delta\nu/\Delta\nu_S$ is equal to the ratio of the total splitting to that caused by the spontelectric field, and second, $U_T - U_L \propto E_S \langle\mu_z\rangle/\mu$, the projection of the spontelectric field, $E_S = \langle E_{\text{asym}} \rangle \langle\mu_z\rangle/\mu$, onto the direction in which the average dipole points. This yields

$$\frac{\Delta\nu}{\nu_T} \approx \frac{(\Delta\nu_S/\Delta\nu)\langle E_{\text{asym}} \rangle(\langle\mu_z\rangle/\mu)^2}{\langle E_{\text{sym}} \rangle[1 + \zeta(\langle\mu_z\rangle/\mu)^2]} + \frac{\Delta\nu_B}{\nu_T} \quad (4)$$

Using the empirical observation that $d\nu_T/d(\langle\mu_z\rangle/\mu) \sim -d\nu_L/d(\langle\mu_z\rangle/\mu)$, the differential of (4) with respect to $\langle\mu_z\rangle/\mu$ gives:

$$\frac{d\nu_T}{d\langle\mu_z\rangle/\mu} = \frac{\langle E_{\text{sym}} \rangle \langle E_{\text{asym}} \rangle \left(\langle\mu_z\rangle/\mu \right) (\nu_L - \Delta\nu_B) \{ 2\xi + \langle\mu_z\rangle/\mu \eta \xi' \}}{\left\{ \langle E_{\text{sym}} \rangle \eta + \langle E_{\text{asym}} \rangle \left(\langle\mu_z\rangle/\mu \right)^2 \xi \right\} \left\{ 2\langle E_{\text{sym}} \rangle \eta + \langle E_{\text{asym}} \rangle \left(\langle\mu_z\rangle/\mu \right)^2 \xi \right\}} \quad (5)$$

where $\xi = \Delta\nu_S/\Delta\nu$, $\eta = 1 + \zeta(\langle\mu_z\rangle/\mu)^2$ and $\xi' = d(\Delta\nu_S/\Delta\nu)/d(\langle\mu_z\rangle/\mu)$. Forming the product of eq. 5 with $d\langle\mu_z\rangle/\mu/dT$ in eq. 3 gives $d\nu_T/dT$. Using the approximation $d\nu_T/dT = -d\nu_L/dT$, we obtain on suitable numerical integration the value of $\Delta\nu$ versus T , as desired.

Before this can be accomplished, some value of ξ' must however be adopted. This was conveniently achieved by a simple fitting procedure based on the observed total LO-TO splitting, a value of $\Delta\nu_B$ and corresponding values of $\langle\mu_z\rangle/\mu$ (see Table 1). For $\Delta\nu_B = 13.5 \text{ cm}^{-1}$, as above, this gives $\xi' = 0.399 - 8.02\langle\mu_z\rangle/\mu + 295(\langle\mu_z\rangle/\mu)^2$ for the range $T_{\text{dep}} = 55, 60, 65$ and 70 K and $\xi' = 0.399 + 9.66\langle\mu_z\rangle/\mu - 503(\langle\mu_z\rangle/\mu)^2 + 8.85 \times 10^3(\langle\mu_z\rangle/\mu)^3$ for $T = 75, 80, 85$ and 90 K with very similar results for example with $\Delta\nu_B = 10 \text{ cm}^{-1}$ (see below).

What remains is to insert values of the spontelectric parameters into the product of equations 3 and 5, represent the resulting derivatives $d\nu_T/dT$ or $d\nu_L/dT$ as a polynomial in T and integrate the result. This yields the variation of the LO-TO splitting, $\Delta\nu$, versus deposition temperature, shown in Fig. 3 obtained using the appropriate parameters for *cis*-MF^{2,3} $\langle E_{\text{sym}} \rangle = 1.206 \times 10^7 \text{ V m}^{-1}$, $\langle E_{\text{asym}} \rangle = 1.148 \times 10^9 \text{ V m}^{-1}$, $\zeta = 1.45 \times 10^4$ given above. Fig. 3 shows a satisfactory agreement between model and observation. We stress that this agreement is the result of the use of analytical forms with proscribed experimental parameters and does *not* represent a ‘fit’ to experimental data.

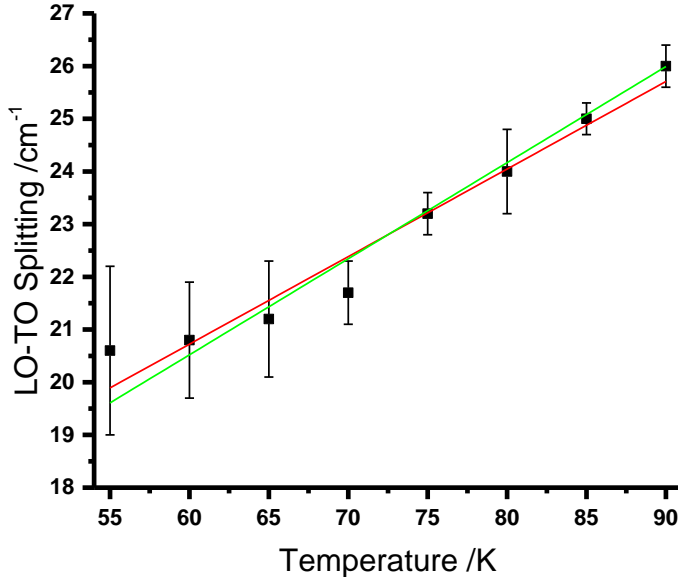


Fig. 3. Comparison between the model, derived from eqns. 3 and 5, (green and red lines) and the observed LO-TO splitting (black squares) with respect to deposition temperature. Two sets of results are shown for $\Delta\nu_B = 10$ and 13.5 cm^{-1} , green and red respectively. Uncertainties in the temperature are of the order of the size of the symbols in the figure, that is, $\pm 0.25 \text{ K}$. For a discussion of the uncertainties shown in the calculated values of the LO-TO splitting, see text.

The greatest source of numerical uncertainty in the calculated values of the LO-TO splitting, shown in Figure 3, is the uncertainty in the value of $\Delta\nu_B$, the inherent LO-TO splitting. $\Delta\nu_B$ may assume a different value from the average observed value for >90 K of ~ 13.5 cm^{-1} , since $\Delta\nu_B$ is structure dependent and MF crystallizes at >90 K.^{15,16} The dependence of the LO-TO splitting on $\Delta\nu_B$ analytically contains the total derivative governing the variation of the degree of dipole orientation with temperature, shown in eq. 3. Any choice of $\Delta\nu_B$ which brings us close to associated singularities yields numerically unreliable results for the LO-TO splitting and thus one may not freely vary the value of $\Delta\nu_B$. With this in mind, an uncertainty of, say, 3.5 cm^{-1} in $\Delta\nu_B$ yields an uncertainty in the calculated LO-TO splitting of ≤ 0.5 cm^{-1} . In order to illustrate this, two estimates of the LO-TO splitting are shown in Figure 3, for $\Delta\nu_B = 10$ and 13.5 cm^{-1} . Note that a lower value of $\Delta\nu_B$ is consistent with a larger unit cell in amorphous, as opposed to crystalline, MF.

4. Conclusions

The significance of the current work is that it underpins the non-linear and non-local nature of the spontelectric effect, as described by equations 1 and 2. These equations through eq. 3, which is derived directly from equation 1 and 2, can predict an *increase* in dipole ordering with increasing deposition temperature. This is represented by a positive value of the rate of change of $\langle\mu_z\rangle/\mu$ with deposition temperature, for a certain range of values of the spontelectric parameters, $\langle E_{\text{sym}}\rangle$, $\langle E_{\text{asym}}\rangle$ and ζ . The goal here was to provide independent data for this surprising phenomenon of the observed growth of dipole order with increasing temperature reported previously.^{2,3} Results in figure 3 show that the parameters which define the spontelectric effect in *cis*-MF, obtained in earlier work based on the e-beam technique and derived using equations 1 and 2, can be used to reproduce the observed temperature dependence of LO-TO splitting measured in RAIR spectroscopy of *cis*-MF. This provides the independent evidence which we seek.

This study is an illustration of how the mathematical structure of a model can lead to new physics. The nature of the spontelectric state suggests a description in terms of an electric field and the Langevin equation, yielding a model which is successful in reproducing the variation of the spontelectric field with deposition temperature for a variety of materials, such as N_2O or the three chlorofluorocarbons CF_3Cl , CF_2Cl_2 , CFCl_3 .³ This description then throws up unusual mathematical properties which turn out to reproduce the observation of quite unexpected behaviour in *cis*-MF. This behaviour was not used as a basis for the model: indeed it was quite unknown when the model was put forward. In this sense the mathematical analysis has become the vehicle through which new physics was explored

Present data illustrate that spontelectrics provide a nanoscopic example of a realisable state of matter, whose properties are described by a continuous function, which is non-differentiable at a set of points in parameter space and in which the state of a system can show discontinuity in response to a continuous influence. Results in earlier work were sufficiently puzzling that we sought and have presented independent experimental evidence which places our description of the spontelectric state upon a very sound basis. With regard to a qualitative understanding of what is afoot here, species as they attach from the gas phase to the surface evidently find it favourable at all temperatures to form a dipole-oriented structure. The formation of such structures is enhanced by weakly hindered diffusion and less restriction to rotation of the molecular constituents. Greater freedom of motion in higher temperature films implies that species are able to explore a greater volume of phase space, overcoming barriers of frustration imposed by $\langle E_{\text{sym}}\rangle$ and ζ between metastable states. Less frustrated

rotation concurrently may allow molecules more readily to align and more than offset the increased disorderly motion associated with higher temperature. This in turn increases the degree of dipole alignment that can be achieved in the system at higher deposition temperatures. This description calls for verification with a dynamical model which describes how the spontelectric state may be established and maintained.

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